ARKIV FÖR FYSIK Band 12 nr 9

Communicated 5 December 1956 by O. Klein and I. Waller

On the calculation of lattice vibrations in KCl

By E. Tenerz

With 4 figures in the text

SUMMARY

The aim of this investigation is to estimate the distribution function of lattice vibrations at 0°K in KCl. Earlier Iona (1941) determined it from the elastic constants and the residual ray frequency measured at room-temperature using the classical Born model. This computation is recalculated with new empirical constants measured at 293°K. Since the residual ray frequency is not known at 0°K, the Born model according to Iona cannot be used in the calculation of the distribution function at 0°K. Therefore we use a modified model where the classical ionic charge is replaced in the Coulomb interaction by an effective charge, which Lundqvist (1955) studied in a quantum mechanical investigation. The specific heat c_v and the Debye temperature θ_D are computed from this distribution function. The agreement between the calculated values of θ_D and the experimental values at low temperatures is not so good as that obtained by Iona. In a preliminary calculation the agreement seems to be better if the polarization, here excluded, is also taken into account.

Introduction

The distribution function of thermal vibrations in ionic crystals has earlier been calculated in connexion with investigations of the specific heat at low temperatures. Kellermann [10] estimated it for NaCl and Iona [8] for KCl, both using the classical Born model. More recently Lundqvist [12] investigated the possibilities of calculating the vibrations from the quantum mechanical expression for the binding energy in the Heitler–London approximation.

Some inaccuracy seems, however, to exist in Iona's and Kellermann's calculations, because they used the elastic constants measured at room-temperature instead of those measured at 0°K, which have to be used in order to compare the theoretical results of the specific heat c_v with the experimental ones. The empirical constants have later been more carefully measured. On account of this a closer investigation of their results seems to be necessary, because their calculations have often been referred to in experimental measurements of c_v at low temperatures.

Our investigation follows in the main the preceding ones. The forces acting upon the ions are regarded as central forces and the KCl lattice as a simple cubic lattice. The purpose is to recalculate Iona's results with better empirical constants. The coefficients in the equation of motion are determined by the elastic constants, the equilibrium condition and the residual ray frequency, by taking into account the repulsive forces from the nearest and the next nearest neighbours.

The aim is to determine the distribution function at 0°K, because the largest deviation between the experimental values of c_v and those calculated with the Born model can be expected in the region where the temperature is below 50°K. At present it is, however, impossible to use the Born model according to Iona, because the residual ray frequency has only been measured at room-temperature. In order to calculate a distribution function at 0°K we use a simplified approach by introducing an effective charge e^* and consider the repulsive forces only between the nearest neighbours.

The effective charge has been investigated by Szigeti [18] and more recently by Lundqvist [12] and [13]. Although the concept of an effective charge was introduced only in connexion with the long polar oscillations, it follows from Lundqvist's investigation that to a certain degree of approximation the same effective charge can be used for all modes of vibrations in the special case of KCl.

Computations by this method are first done at room-temperature in order to make a comparison with the calculation according to Iona's scheme. The comparison shows that the transverse branches change very little and the longitudinal branch is cut down to a better agreement with the value calculated from electromagnetic theory.

Lastly we estimate the distribution function at 0°K with the method sketched. From the distribution function c_v the Debye temperature θ_D is determined. θ_D is not in good agreement with the experimental result when the temperature is above 10°K, which may be due to the polarization which is not taken into account here. A preliminary calculation shows that the frequencies seem to decrease generally if it is included. Thus the distribution function is displaced to smaller frequencies, the specific heat increases, and the Debye temperature decreases, in better agreement with the experiment.

The frequency spectrum

The KCl lattice is assumed to be a simple cubic lattice with equal masses for K^+ and Cl^-. The forces acting upon the ions are regarded as central forces. In this case the Cauchy relation $c_{12} = c_{44}$ is fulfilled. For KCl and NaCl the deviation is not so large. Löwdin [15] first showed that this deviation may depend on many-body forces which he separated and found to be of importance in explaining the difference between c_{12} and c_{44}. In our calculation the mean value of c_{12} and c_{44} is used.

The potential energy is expanded in powers of the displacements from the equilibrium position and the second order term is put in the equation of motion. Looking for plane wave solutions with the frequency ω and the amplitude U we obtain

$$m\,\omega^2 U_x = -\sum_y A_{xy} U_y \quad \text{(three equations)}, \tag{1}$$

where m is the mass and the A_{xy} are given from the derivatives of the potential energy of the ion in the direction of x and y.

We divide the potential energy into two parts, one electrostatic and one due to the repulsive forces. Accordingly the coefficients A_{xy} are divided into two parts $A_{xy} = A^e_{xy} + A^r_{xy}$. Iona has calculated A^e_{xy} from a formula given by Waller for a simple cubic crystal. A^r_{xy} can be estimated from the force constants P and Q according to Born [1] and Born and Göppert-Mayer [2], when the elastic constants are known. One relation is obtained from the equilibrium condition. When the repulsive forces from both the nearest and the next nearest neighbours are included, another relation is necessary. This can be obtained from the residual ray frequency.

In our calculations an effective charge e^* is introduced. It has been investigated by Szigeti [18] and more recently by Lundqvist [12, 13]. Szigeti deduced an expression for it using macroscopic theory and obtained a formula containing empirical constants. For the alkali halides he found that e^*/e is smaller than unity and for KCl equal to 0.80 when the empirical constants at room-temperature are used.

Lundqvist [12] considered the quantum mechanical expression for the binding energy in the Heitler–London approximation. He used the formulas for the binding energy of an ionic crystal, which are based on a work by Hylleraas [7] and developed by Landshoff [11] and later discussed in great detail by Löwdin [15]. In the approximation considered by Lundqvist, the potential energy contains both two-body interaction and also many-body interactions. He pointed out that these many-body terms lead to the introduction of an effective charge. He derived a formula, which is related to the elastic constants c_{12} and c_{44}, from an approximate expression for the three-body potential and obtained the value 0.86 for KCl when the elastic constants at 0°K are used. Later [13] he improved the approximation for the three-body potential, giving rise to certain correction terms in the effective charge. The expressions for the coefficients were derived only for the long polar vibrations but from these expressions the behaviour at other frequencies is clear. If the residual ray frequency were known at 0°K it would be possible to deduce a good value for e^* from it, but so far it has only been measured at room-temperature. When the Cauchy relation is valid one gets a good result for e^* from c_{12}, but the larger the deviation, the worse is the result. Although the effective charge generally is a rather complicated effect, one can take it into account for the special case of KCl in an approximate way simply by replacing the classical ionic charge by an effective charge in the Coulomb interaction, because the deviation from the Cauchy relation is small for KCl. For KCl at 0°K $c_{12} = 0.6 \times 10^{11}$ dyn/cm^2 and $c_{44} = 0.669 \times 10^{11}$ dyn/cm^2. This deviation may depend on many-body forces, which are neglected in our calculations, and the mean value of c_{12} and c_{44} is used. The effective charge is estimated from the expression for c_{12} when the repulsive forces from only the nearest neighbours are taken into account. In that case only the electrostatic part of the coefficients contributes to c_{12} and the expression for it is according to Löwdin [14]

$$c_{12} = \frac{3\,e^{*2}}{2\,a^4}\,0.2318. \tag{2}$$

The value obtained for e^*/e is 0.86 at 0°K and the same at 293°K.[1]

In one of our investigations we use Szigeti's value and consider the interaction between the nearest and the next nearest neighbours. In this case we have no theoretical justification for the calculation and we wish only to see how the frequencies are affected.

The calculations are done for five different cases:

---

[1] This formula is approximately correct only for a static lattice. For the present work, however, it will be assumed to be valid for arbitrary temperatures, in order to give the correct elastic waves. Corresponding assumptions seem to have been made in all calculations of lattice vibrations. As far as we know, no theoretical justification for such assumptions has been given.

A. At 293°K with the repulsive forces from the nearest and the next nearest neighbours and $e^*/e = 1$.
B. At 293°K with the repulsive forces from the nearest neighbours and $e^*/e = 0.86$.
C. At 0°K with the repulsive forces from the nearest neighbours and $e^*/e = 0.86$.
D. At 0°K with the repulsive forces from the nearest neighbours and $e^*/e = 1$.
E. At 293°K with the repulsive forces from the nearest and the next nearest neighbours and $e^*/e = 0.80$.

See Table 1.

Table 1. Values of the frequencies.

μ_x	μ_y	μ_z	A			B			C			D			E		
			$\omega_1 \times 10^{-13}$	$\omega_2 \times 10^{-13}$	$\omega_3 \times 10^{-13}$	$\omega_1 \times 10^{-13}$	$\omega_2 \times 10^{-13}$	$\omega_3 \times 10^{-13}$	$\omega_1 \times 10^{-13}$	$\omega_2 \times 10^{-13}$	$\omega_3 \times 10^{-13}$	$\omega_1 \times 10^{-13}$	$\omega_2 \times 10^{-13}$	$\omega_3 \times 10^{-13}$	$\omega_1 \times 10^{-13}$	$\omega_2 \times 10^{-13}$	$\omega_3 \times 10^{-13}$
0	0	$\frac{1}{4}$	1.09	0.44	0.44	1.09	0.43	0.43	1.21	0.43	0.43	1.21	0.51	0.51	1.09	0.43	0.43
0	0	$\frac{1}{2}$	1.99	0.83	0.83	2.00	0.80	0.80	2.22	0.81	0.81	2.22	0.95	0.95	2.00	0.80	0.80
0	0	$\frac{3}{4}$	2.59	1.10	1.10	2.60	1.06	1.06	2.89	1.08	1.08	2.88	1.25	1.25	2.61	1.06	1.06
0	0	1	2.79	1.20	1.20	2.81	1.16	1.16	3.12	1.17	1.17	3.11	1.36	1.36	2.82	1.16	1.16
0	$\frac{1}{4}$	$\frac{1}{4}$	1.30	1.01	0.68	1.29	1.01	0.65	1.39	1.14	0.66	1.45	1.10	0.77	1.29	1.01	0.65
0	$\frac{1}{4}$	$\frac{1}{2}$	2.04	1.30	1.07	2.04	1.28	1.02	2.25	1.39	1.03	2.27	1.44	1.20	2.04	1.28	1.01
0	$\frac{1}{4}$	$\frac{3}{4}$	2.59	1.49	1.38	2.60	1.46	1.30	2.89	1.56	1.32	2.88	1.66	1.53	2.61	1.46	1.29
0	$\frac{1}{4}$	1	2.78	1.57	1.50	2.79	1.53	1.41	3.11	1.62	1.42	3.09	1.75	1.66	2.80	1.53	1.39
0	$\frac{1}{2}$	$\frac{1}{2}$	2.26	1.89	1.55	2.23	1.88	1.43	2.43	2.11	1.45	2.50	2.07	1.68	2.23	1.89	1.41
0	$\frac{1}{2}$	$\frac{3}{4}$	2.62	2.11	1.94	2.61	2.09	1.79	2.89	2.31	1.80	2.89	2.32	2.10	2.61	2.09	1.75
0	$\frac{1}{2}$	1	2.76	2.18	2.10	2.76	2.14	1.92	3.07	2.35	1.94	3.04	2.39	2.26	2.77	2.14	1.88
0	$\frac{3}{4}$	$\frac{3}{4}$	2.67	2.50	2.44	2.62	2.51	2.21	2.93	2.78	2.24	2.93	2.74	2.60	2.66	2.50	2.15
0	$\frac{3}{4}$	1	2.73	2.63	2.59	2.72	2.57	2.38	3.04	2.85	2.41	2.99	2.83	2.80	2.73	2.57	2.31
0	1	1	2.84	2.72	2.72	2.56	2.71	2.71	2.59	3.02	3.02	3.01	2.97	2.97	2.49	2.72	2.72
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.57	1.07	1.07	1.53	1.07	1.07	1.63	1.19	1.19	1.75	1.19	1.19	1.53	1.08	1.08
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	2.18	1.57	1.23	2.14	1.52	1.22	2.33	1.64	1.33	2.41	1.71	1.37	2.14	1.51	1.23
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	2.63	1.96	1.38	2.62	1.85	1.36	2.90	1.95	1.46	2.91	2.13	1.54	2.62	1.83	1.37
$\frac{1}{4}$	$\frac{1}{4}$	1	2.77	2.12	1.44	2.78	1.99	1.42	3.09	2.07	1.52	3.07	2.30	1.61	2.79	1.95	1.43
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	2.57	1.90	1.62	2.47	1.89	1.57	2.64	2.12	1.69	2.81	2.08	1.77	2.44	1.90	1.57
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	2.85	2.36	1.81	2.71	2.29	1.76	2.99	2.50	1.89	3.09	2.57	1.99	2.72	2.29	1.77
$\frac{1}{4}$	$\frac{1}{2}$	1	2.76	2.75	1.86	2.74	2.57	1.82	3.06	2.71	1.97	3.02	2.95	2.04	2.76	2.52	1.83
$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	3.10	2.49	2.33	2.91	2.48	2.24	3.13	2.78	2.38	3.32	2.73	2.53	2.87	2.50	2.22
$\frac{1}{4}$	$\frac{3}{4}$	1	3.13	2.72	2.41	2.89	2.71	2.35	3.07	3.03	2.53	3.32	2.98	2.62	2.83	2.73	2.34
$\frac{1}{4}$	1	1	3.19	2.71	2.71	2.87	2.69	2.69	2.95	3.01	3.01	3.35	2.96	2.96	2.78	2.71	2.71
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.11	1.93	1.93	2.92	1.92	1.92	3.09	2.15	2.15	3.34	2.11	2.11	2.87	1.94	1.94
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	3.43	2.42	1.96	3.18	2.40	1.95	3.37	2.67	2.17	3.64	2.64	2.15	3.11	2.41	1.97
$\frac{1}{2}$	$\frac{1}{2}$	1	3.45	2.72	1.98	3.16	2.71	1.96	3.33	3.03	2.18	3.63	2.98	2.16	3.08	2.73	1.99
$\frac{1}{2}$	$\frac{3}{4}$	$\frac{3}{4}$	3.80	2.48	2.31	3.48	2.46	2.28	3.68	2.76	2.53	3.99	2.70	2.51	3.39	2.49	2.30
$\frac{1}{2}$	$\frac{3}{4}$	1	3.86	2.70	2.37	3.50	2.68	2.35	3.68	3.00	2.62	4.02	2.94	2.58	3.40	2.71	2.38
$\frac{1}{2}$	1	1	3.90	2.67	2.67	3.50	2.66	2.66	3.67	2.98	2.98	4.05	2.92	2.92	3.39	2.69	2.69
$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	4.28	2.48	2.48	3.90	2.44	2.44	4.12	2.74	2.74	4.47	2.68	2.68	3.78	2.48	2.48
$\frac{3}{4}$	$\frac{3}{4}$	1	4.39	2.68	2.47	3.97	2.64	2.44	4.19	2.97	2.73	4.55	2.90	2.67	3.84	2.69	2.48
$\frac{3}{4}$	1	1	4.50	2.67	2.67	4.04	2.63	2.63	4.26	2.96	2.96	4.65	2.88	2.88	3.81	2.68	2.68
1	1	1	4.72	2.67	2.67	4.25	2.62	2.62	4.49	2.95	2.95	4.87	2.87	2.87	4.10	2.67	2.67

$\mu_\alpha = \varphi_\alpha / \pi$. $(\alpha = x, y, z,)$

In the cases B and C the effective charge is calculated from (2). The elastic constants used have in all cases been measured by Durand [5]. The residual ray frequency is 2.67×10^{13} sec^{-1} at 293°K.

For the specific heat the following relation is valid:

$$C_v = k N \int^{\nu_{\max}} \frac{\left(\frac{h\nu}{kT}\right)^2 e^{h\nu/kT}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2} f(\nu)\, d\nu, \tag{3}$$

where N is the number of the oscillators, k Boltzmann's constant, h Planck's constant, ν are the frequencies of the oscillators, and $f(\nu)$ is the distribution function of lattice vibrations.

In order to use this formula it is necessary to know the distribution function, which is computed in the following way. The frequencies are determined from the equations (1). Because the KCl lattice is regarded as a simple cubic lattice, the determinant gives a third degree equation in ω^2 from which ω can easily be found. From the determinant three positive, in general different, values of ω are found. In Table 1 these are arranged in three branches of vibrations, one containing the highest, one the intermediate, and one the lowest frequencies. In order to calculate the distribution function we interpolate the frequency midway between two calculated points. This is possible by constructing three smooth surfaces, one for each branch in the $\varphi_x\, \varphi_y\, \varphi_z\, \omega$ space, where $\varphi_x\, \varphi_y\, \varphi_z$ are the components of the wave vector. Thus we obtain the frequencies at the points where $\varphi_x = n\pi/8$, $\varphi_y = m\pi/8$, $\varphi_z = l\pi/8$ (n, m, l integers).

The whole frequency range is divided into 24 intervals, and the number of calculated frequencies in each interval is counted. Finally we normalize the distribution function so that

$$\int f(\nu)\, d\nu = 3. \tag{4}$$

Table 1 gives the frequencies in the different cases.

The frequencies are calculated at 293°K with the Born model according to Iona. A comparison between Iona's results and ours shows how a change of the elastic constants alters the result. Iona used the elastic constants measured by Försterling [6] which are $c_{11} = 3.767 \times 10^{11}$ dyn/cm^2 and $c_{12} = 0.633 \times 10^{11}$ dyn/cm^2, while we use $c_{11} = 4.00 \times 10^{11}$ dyn/cm^2 and $c_{12} = 0.616 \times 10^{11}$ dyn/cm^2. Our frequencies are in general somewhat higher than Iona's.

The aim of the investigation is to determine the distribution function at 0°K, but as long as the residual ray frequency is not known at 0°K, we cannot use the Born model according to Iona. For this reason an effective charge is introduced which is estimated from c_{12} and the repulsive forces between nearest neighbours only are taken into account. A comparison between this calculation at room-temperature and the preceding one shows that the agreement for the transverse branches is good and that the limiting frequency for the longitudinal branch is in better agreement with the value 3.96×10^{13}, which is obtained from the dielectric constants. It confirms the assertion that the frequencies will be nearly the same when only the nearest neighbours are considered for the repulsive parts of the coefficients and when the effective charge is computed from the experimental values of c_{12}. For this reason a calculation at 0°K is done with an effective charge and the repulsive forces from the

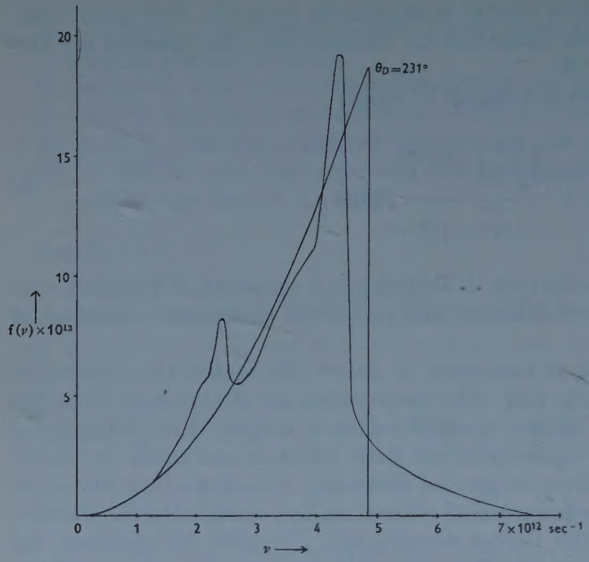

Fig. 1. The distribution function calculated from the frequencies of table 1 A.

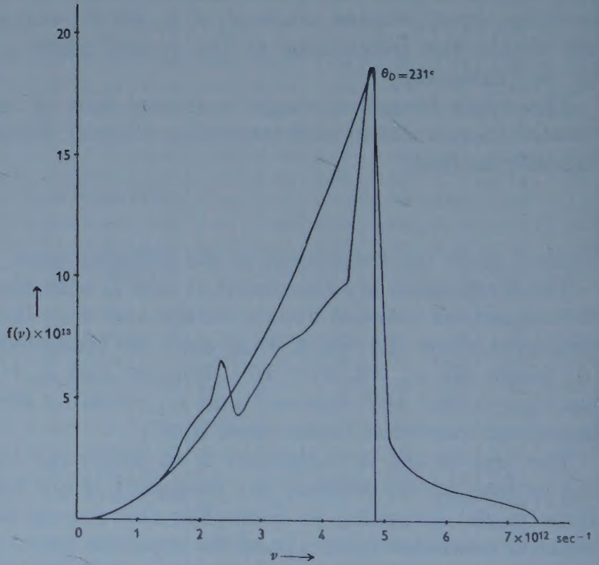

Fig. 2. The distribution function calculated from the frequencies of table 1 C.

nearest neighbours only. We see that the limiting frequencies at 0°K are in good agreement with the values obtained by Lundqvist.

Figs. 1, 2 and 3 show the distribution function in three different cases. From them one can see that the highest maximum of the functions moves to higher frequencies when the temperature decreases. The maximum lies at the residual ray frequency, and when the temperature decreases, the residual ray frequency moves to higher

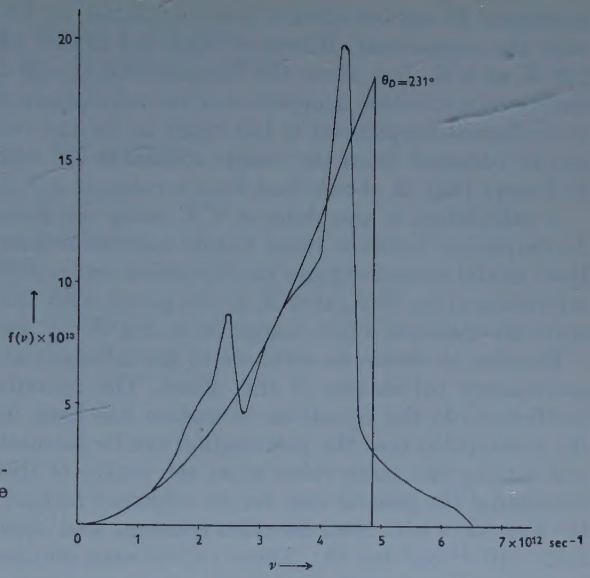

Fig. 3. The distribution function calculated from the frequencies of table 1 E.

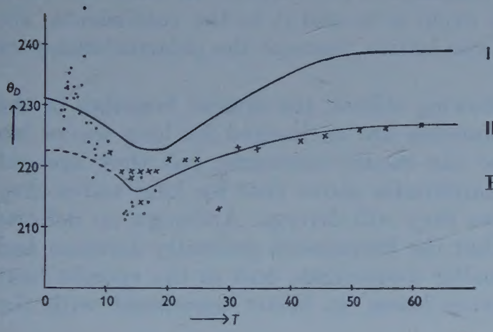

Fig. 4. Debye's characteristic temperature.

+ – Clusius, Goldmann and Perlick [4].
• – Keesom and Clark [9].
I – calculated from fig. 2.
II – calculated by Iona.

values, and so the peak too is moved.[1] We can also see that the first peak is not as high at 0°K as at 293°K. This peak has a great importance in the calculation of c_v at low temperatures.

A comparison between the zero-point energy calculated with Debye's distribution function and that calculated with ours at 0°K shows that the Debye model gives 1.03 kcal/mole and ours 1.09 kcal/mole. The difference is only 6 %.

When the specific heat is known, Debye's characteristic temperature can be computed. This is done with the distribution function at 0°K. As Fig. 4 shows, the deviation from the values found by experiment is greater than that found by Iona when the temperature is above 10°K. However, he used the distribution function at room-temperature, and assumed that it does not change when the temperature decreases. If our calculation is extrapolated to $T < 10°K$, it is in better agreement with the experiment. However, Iona has drawn his curve so that it points to $\theta_D = 230°K$ at 0°K, but when the temperature is below 10°K, a very small part of the distribution function is included in the calculation of c_v, and in this region the number of evaluated frequencies is too small to fix the curve. The value at 0°K, however, can be obtained from the elastic constants by means of cubic harmonics according to Tenerz [19]. It shows that Iona's value at 0°K is appreciably lower.

---

[1] An attempt has been made to calculate the heights of the peaks by means of the method given by van Hove [20] (cf. also Rosenstock [16]). The coefficients are not, however, given as analytical expressions in our investigation and the possibilities of estimating an approximate expression for the coefficients are limited by the roughness of the network.

A calculation is also done at 0°K using the Born model and the classical charge. A comparison between these results and the results when e^* is used, shows that the Born model cannot explain the deviation between the theoretical and the experimental values of θ_D. If θ_D at 0°K is computed with the values for c_{12} obtained from (2) with the classical ionic charge, it is 254°K by the method with kubic harmonics.

In order to obtain an estimate of the influence of the polarization we have done a preliminary calculation of this effect. The contribution of the polarization to the coefficients in the equations of motion has been deduced by Lundqvist [13] under the assumption that the polarization can be calculated as if the field were homogeneous, having the same value as at the centre of the ions. Born and Huang [3] have considered the general case for an arbitrary lattice. The electronic polarizabilities of the ions have here been assumed constant and equal to 1.13×10^{-24} cm^3 for K^+ and 2.92×10^{-24} cm^3 for Cl^-. These values were obtained by Shockley [17]. The contribution from the polarization to the elastic constants is zero, and so the force constants will not change. The only thing we have to do is to add it to the coefficients. We cannot, however, regard KCl as a one-atomic lattice, because the polarizabilities for K^+ and Cl^- are not the same.

The polarization seems to have the following effects: the optical branches of the frequencies are cut down; the acoustic branches are unchanged for long waves because the polarization does not influence the elastic constants, but they are cut down for shorter waves. A study of the amplitudes shows that for long waves they are equal, but when the waves are shorter they will diverge. Although no definite conclucions can yet be drawn, it seems that the frequencies generally decrease and the distribution function is pushed to smaller frequencies, and so the specific heat will be greater and the Debye temperature lower, in better agreement with the experiment.

I wish to express my gratitude to Professor I. Waller for suggesting this investigation and for much helpful advice. I am also indebted to Dr. S. O. Lundqvist for many valuable discussions and comments. The work has partly been supported by the Swedish Natural Research Council.

Institute of Theoretical Physics, University of Uppsala.

REFERENCES

1. Born, M., Atomtheorie des festen Zustandes. Leipzig 1923.
2. Born. M., and Göppert-Mayer, M., Handbuch der Physik *24* (2), 623 (1933).
3. Born, M., and Huang, K., Dynamical Theory of Crystal Lattices. Oxford (1954).
4. Clusius, K., Goldmann, J., and Perlick, A., Zeit. f. Naturf. *4a*, 424 (1949).
5. Durand, M. A., Phys. Rev. *50*, 449 (1936).
6. Försterling, K., Zeit. f. Phys. *2*, 172 (1920).
7. Hylleraas, E. A., Zeit. f. Phys. *63*, 771 (1930).

8. Iona, M., Phys. Rev. *60,* 822 (1941).
9. Keesom, W. H., and Clark, C. W., Physica *2,* 698 (1935).
10. Kellermann, E. W., Phil. Trans. Roy. Soc. *238,* 513 (1940).
11. Landshoff, R., Zeit. f. Phys. *102,* 201 (1936).
12. Lundqvist, S. O., Ark. Fys. *9,* 435 (1955).
13. —— Ark. Fys. *12,* 263 (1957).
14. Löwdin, P. O., Ark. f. mat. fys. astr. *35A,* 9 (1948).
15. —— Thesis, Uppsala 1948.
16. Rosenstock, H. B., Phys. Rev. *97,* 290 (1955).
17. Shockley, W., Phys. Rev. *70,* 105 (1946).
18. Szigeti, B., Trans. Faraday Soc. *45,* 155 (1949).
19. Tenerz, E., Ark. Fys. *11,* 247 (1956).
20. Van Hove, L., Phys. Rev. *89,* 1189 (1953).

Tryckt den 17 maj 1957

Uppsala 1957. Almqvist & Wiksells Boktryckeri AB